HIGH TEMPERATURE HARD ANODIZING OF ALUMINUM IN ORGANIC ELECTROLYTES

by

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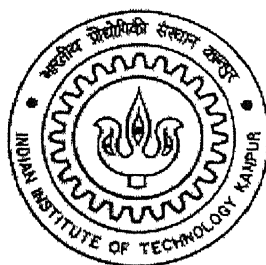
ALUMINUM IN ORGANIC ELECTROLYTES

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By

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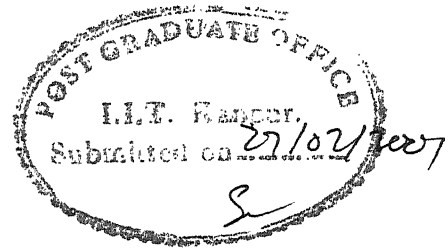
CERTIFICATE

This is to certify that the work contained in the thesis entitled " **High temperature hard anodizing of aluminum in organic electrolytes**" submitted by **Rajesh Sisodia** (**Roll No. 9910616**) has been carried out under our supervision and to best of our knowledge this work has not been submitted elsewhere for degree.

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ABSTRACT

An aluminum alloy of composition (Al 98.477%, Fe 1.16%. Si 0.334% and

Cu 0.028%) was hard anodized in binary acid solutions viz. tartaric acid, maleic acid or

malonic acid (1.0 mole/l and 2.5mole/l) mixed with oxalic acid (0.17 mole/l) for

anodizing time varied from 10 to 60 minutes, by applying current densities of 5A/dm^2

and 10A/dm^2 at room temperature. The effect of addition of oxalic acid on the bath

voltage, hardness of the film and coating ratio were studied˙ The addition of oxalic acid

increases the conductivity of the bath, thereby reducing the bath voltage. A uniform,

integral colored, crack free and hard oxide films of 375 to 485VHN were formed in these

solutions. Hardness values generally increases with decreasing the oxalic acid

concentrations of the bath. The coating ratio was found to be higher for higher

concentrations baths of base acid and also for higher current densities values. Also, the

properties of the anodized sample under stirring conditions was found to better than

under non-stirring conditions. From these results, the anodizing characteristics of

aluminum in these baths were found to be essentially the same as that in sulphuric and

oxalic acid bath.

CHAPTER -1

INTRODUCTION

The practice of anodizing or controlled oxidation, of aluminum and aluminum alloys is more than seven decades old. When aluminum is exposed to atmosphere, a tenacious oxide film is formed on it. This natural oxide film can be thickened by anodizing. The primary intent of anodizing aluminum and aluminum-alloys parts is to protect the highly reactive surface against corrosion in aqueous environments, such as, humid air and sea water. Because the anodic coating can be produced in a variety of colors, painted anodized parts are used in architectural applications. The search for denser, heavier and hard coatings led to the development of hard anodizing. The first reference to hard anodizing dates back to 1946. However, regular commercial practice appears to have started around 1956. Since that time the progress has been quite significant and this process has gained wide commercial applications[1].

1.1 Aim of the investigation:

Hard anodizing is an electrolytic oxidation process utilized to obtain a hard coating of Al_2O_3 layer on a variety of aluminum alloys. This coating has many advantages as compared to oxide coating produced by conventional anodizing process. These include greater thickness, higher hardness and corrosion resistance. The hard coating on aluminum makes it possible to use light metal in many applications, formerly restricted to steel for wear and abrasive situations.

These hard anodizing processes have been usually carried out at a temperature between -5^0C to 5^0C. Maintaining of such low temperatures, however, requires special facilities for refrigeration. In a country, such as India, where the temperature through out

the year is around 30^0C and above, such, a process is commercially undesirable because erecting refrigeration facilities and its maintenance makes the process very expensive. Saving in cost can be achieved, if the hard anodizing is carried out at room temperatures. Many electrolytes have been discovered to produce hard anodic coatings at room temperature. Some of these electrolytes use solutions of organic compounds such as maleic acid, tartaric acid or malonic acid. Electrolytes based on these materials require higher voltage compared to conventional low temperature processes. To overcome this difficulty some additives have been tried. In the present work an attempt have been made to investigate the effect of some organic acid mixtures in various proportions on properties of hard anodic coatings.

1.2 Principle of anodic oxidation:

Anodizing is an electrochemical oxidation process, which is carried out in an aqueous solution to form an oxide layer on the surface of aluminum substrate. The aluminum part to be anodized is connected to the positive terminal of a power source and a non-reactive metal, such as stainless steel, is connected to the negative terminal. When current is passed through the electrolyte, the negatively charged ions(oxygen ions) will migrate towards the anode and positively charged ions(hydrogen ions) will migrate towards the cathode. At cathode, the evolution of hydrogen gas takes place. Most, of the oxygen that would have been liberated combines with the aluminum(anode) to form a layer of porous Al_2O_3. The overall electrochemical reaction involving the conversion of aluminum metal into alumina is:

$$2Al + 3H_2O \rightarrow Al_2O_3 + 3H_2.$$
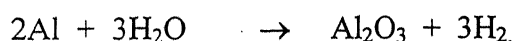
1.2 Classification of oxide coatings:

According to whether or not the electrolyte exerts appreciable solvent action on the oxide, the anodic oxide film are classified into following types:

1.3.1 Non – porous oxide film :

This type of film is formed, when the electrolyte has no solvent action on the film. The reaction products may be almost insoluble in the electrolyte and a strongly adherent and practically non-conducting film is formed on the anode(barrier film). In this case, film growth continues until the resistance of the film prevents the current from reaching the anode. Films formed in this way are extremely thin, non-porous and dielectrically compact and is shown in the Figure1.1. The thickness of the barrier layer film is proportional only to the applied voltage and this relationship is represented in the figure 1.2, as obtained by earlier workers [2]. The maximum theoretical value of barrier layer approaches to a value of 14 A^0/volt The barrier layer formed in anodizing is chemically of the same nature as the natural oxide formed in the atmosphere[3]. This type of film is formed on boric acid, borates or tartrates solutions. This type of film conducts current only due to its thinness and faults in the skeleton and it posses unique electrical properties and therefore have been used extensively in production of electrolytic condensers, capacitors and rectifiers and also for protection of very thin aluminum coatings e.g. those applied by vacuum deposition[4].
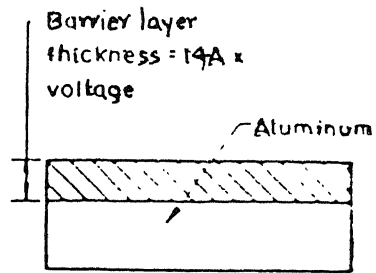
Figure1.1 Barrier type oxide coating
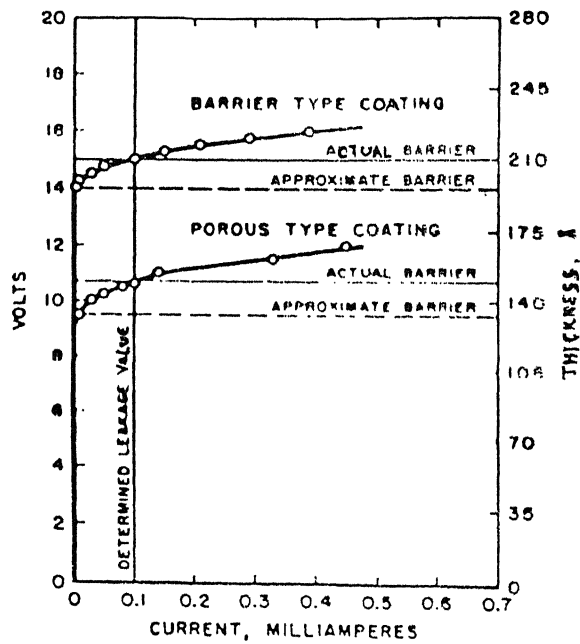
Figure 1.2 Determination of barrier layer thickness.

1.3.2   Semi porous oxide film:

This type of film is formed if the reaction products may be sparingly soluble in the electrolyte and thus a strongly adherent film, which is non-conducting when dry, is formed over the anode. The film growth continues until the resistance of the film prevents the current from reaching the anode. This film growth is accompanied by the localized dissolution of the film. Pores are thus formed in the coating, which are wide enough to allow continuous access of the current to the metal. The growth of the film remains continues. but its rate of formation gets gradually retarded as the film grows thicker and, hence, electrical resistance increases. The process remains continues until a stage is reached at which the rate of formation of film is equal to the rate of dissolution of the film in the electrolyte. At this stage, the film thickness remains constant. The oxide film thus formed is a combination of both inner barrier layer and the outer porous layer and is shown in the Figure 1.3. The thickness of the inner barrier layer is only 0.1 to 2.0% of the total oxide film thickness and it always remains in contact with aluminum metal. In this type of film the maximum theoretical value of barrier layer approaches to a value of 11.5 A^0/volt[2]. The outer thick layer, which is a micro porous layer grows over the thin non-porous layer and is of columnar structure. The maximum film thickness achievable will depend on the nature of the electrolyte and its ability to dissolve the oxide and on the operating conditions.
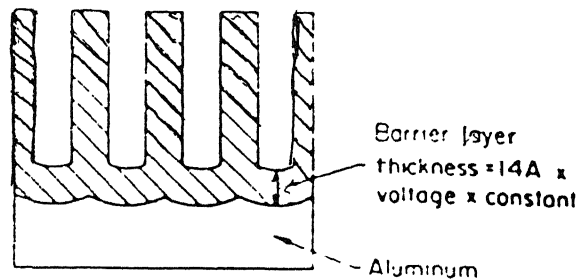
Figure 1.3   Porous type oxide coating.

1.4   Mechanism of electrolytic oxidaton :

Scott Anderson[5] had postulated that oxide growth occurs by virtue of an outward diffusion of aluminum ions from the metal to the solution and an inward diffusion of oxygen ions supplied at the base of the pores by the electrolyte. The mechanism of diffusion process is such that the barrier layer always separates the electrolyte from the metal and the contact between the barrier layer and the metal remains intact. In this way, strongly adherent films are formed.

Initially, when the current passes through the electrolyte the oxygen gets liberated at the anode and oxidation will result. The layer of oxide formed in this way establishes a barrier between the solution and the metal, and further passage of current must take place through this oxide film for its continuous growth and is therefore dependent upon the ability of the aluminum and oxygen ions to penetrate the barrier layer. The aluminum ion

Al^{+3} has a very small radius of $0.5A^{0}$ and it can easily diffuse through the barrier under the influence of the intense electrical field present. This field is of the order of 10^{7} volts/cm. The space within the metal lattice vacated by the Al^{+3} ions provide room that can be filled by the O^{--} ions jumping from positions within the adjacent oxide layer. The oxygen ions have a large radius of the order of $1.3A^{0}$, and can move toward the metal sheet under the influence of the electric field only when sufficient space is provided for them. The oxygen ion positions, in the oxide vacated by ions moving into the space left by the migrating Al^{+3} ions are filled by adjacent O^{--} ions further out in the oxide film. Eventually, the unoccupied O^{--} spaces reach the electrolyte where they are filled by ions from the electrolyte.

It is an observed fact when aluminum is anodically oxidized, the thickness of the oxide is moderately greater than that of the aluminum from which it is formed. Schenk[6] by assuming the closest packing of the oxide, founds that a volume increase of 48% is involved in the change of Al to Al_2O_3 Hence, when an Al^{+3} ion diffuses into the interstices of the oxide, two of the adjacent metal ions, by some adjustment in position, can create vacancies to be filled by oxygen, thus forming Al_2O_3.

In this way, the oxide layer increases in thickness by a stepwise migration of O^{--} ions into spaces in the metal lattice that have been previously vacated by Al^{+3} ions diffusing outward through the oxide into the electrolyte. One out of every three Al^{+3} ions on the surface of the metal diffuses through the oxide leaves the other two to combine with oxygen to form aluminum-oxide(Al_2O_3). In this way the oxide thickness increases, with the barrier layer continuously in good contact with the metal, and strongly adherent thereto.

The mobile Al^{+3} ions, which diffuse from the surface of the aluminum sheet, in effect dissolve into the oxide layer and migrate as a result of the presence of electrical field. Once, with in the oxide film, the positive ion finds a sufficient number of like ions already present to neutralize the charge of the O^{--} ions in the layer. Therefore, it passes on through the layer, diffusing between the ions composing the barrier. When it reaches the electrolyte it forms a soluble compound and enters into the solution. Thus, one out of every three aluminum ions that leaves the parent metal continues and passes through the oxide film into the acid electrolyte. This Al^{+3} ion does not become the part of the aluminum oxide molecule. The continued growth of the film is dependent upon this loss of aluminum ions.

1.5 Structure of the oxide film:

Keller, Hunter and Robinson[4] has found by electron microscopy that the porous coating shows a hexagonal cell structure and the formation of single cell of oxide takes place by virtue of solvent action at a single point. When solvent action begins at this single point, the thickness of the oxide gets reduced and current flows to repair the damage to the oxide layer. This raises the electrolyte temperature at this point and more rapid dissolution of oxide occurs. This mechanism would lead to the perpetuation of a pore once it is formed. As current continues to flow through the single pore under consideration and additional oxide forms, it is evident that an oxide cell must be created. Because the voltage and current fields about a point tend to be spherical, the advancing front of the oxide cell would be spherical if the pore was actually a point source. Since the pore is of finite size, however, the cell front will have the shape of a spherical section

somewhat less than a hemisphere. Thus, as oxide is formed, a cylindrical cell, having a roughly hemispherical end and a central cylindrical pore, will be formed. In actual practice, however, a continuous compact oxide layer rather than isolated ideal cell is formed. At the start of coating formation, the ideal cells probably do start to form, but if only cylindrical cells formed, intervening pillars of metal would remain. These pillars would still be in the effective electrical circuit and therefore would be converted to oxide. In such a closed packed array of cylinders, each cylinder would have a line contact with six surrounding cylinders and between each group of three contacting cylinders there would be a triangular pillar of metal with concave surfaces. As these pillars are converted to oxide anodically, the metal will be consumed equally from each face under the influence of the current from the pores of the three surrounding cells. When the entire metal pillar is consumed in this fashion, the oxide layer will be continuous and the cells will have the form of hexagonal prisms rather than cylinders. With this conversion of the ideal cylindrical cell to the actual close packed array of hexagonal cells, changes in the shape of the pore also must occur and the enlargement of the pore takes place in proportion to the amount of metal consumed. Thus, the pore will no longer be cylindrical, but will have six projections, each directed toward a corner of the hexagon. The cross-section of this shape should be roughly that of a six-pointed star, which will vary somewhat in shape according to the size of the pore. The relationship between the cylindrical structure and the hexagonal cell structure is shown in Figure 1.4. The front of a single cell in a close-packed array will have a larger radius of curvature than that of a single isolated cell, and the cell front will have the shape of the spherical section somewhat less than a hemisphere.
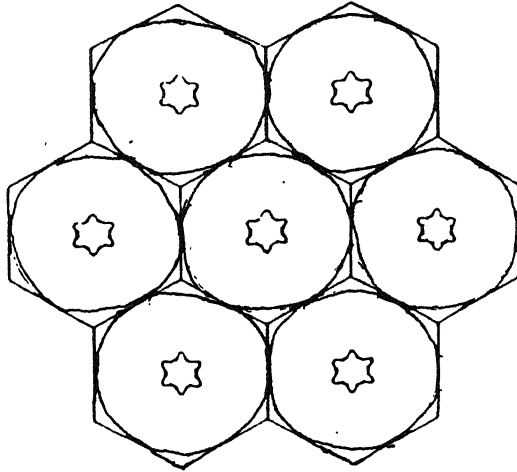
Figure 1.4 Relation between ideal cylindrical oxide cells with cylindrical pores and close-packed hexagonal cells with star shaped pores.

1.6 Type of anodizing processes:

The anodizing processes employed for the formation of semi- porous oxide coatings are divided into following types:

a.) Normal Anodizing

b.) Continuous anodizing.

c.) Integral color anodizing.

d.) Hard Anodizing.

e.) Microplasmic anodizing.

Normal or traditional anodizing is used for achieving a uniform and smooth finishing, for corrosion and wear resistance, for coloring and for facilitating adhesion of paints and lacquers. The thickness of the film obtained by this process is of

the order of 5 – 25 μm. The electrolytic bath used for normal anodizing comprise aqueous solutions of chromic-acid, ortho phosphoric acid, sulfuric acid, oxalic acid or combination there of. The potential difference is of the order of 20 – 100V and the current density is between 1-10mA/cm^2.

Continuous anodizing process is mainly used for the anodizing of long lengths of wire, strip and foil. The operating conditions and solutions are fundamentally same, as for ordinary sulphuric acid anodizing, but as the aluminum moves at a constant speed, the effective bath length predetermines the time of dwell in each bath. The maximum anodic film thickness obtainable is usually about 2-6μm.

Integral color anodizing process, results in the production of oxide films whose abrasion resistant is twice the normal sulphuric acid films and can be produced in a range of colors from pale yellow through bronze to black. The electrolyte used for this process, covers a wide range of organic acid solutions, usually containing small additions of sulphuric acid. The precise color produced by a given integral process depends upon the alloy-composition. These processes had been widely used for architectural work such as windows, shop frames and curtain walling and the integral colors are exceptionally light fast and can confidently be specified for prolonged outdoors exposure.

Hard anodizing is a term used to describe the production of anodic coatings with film hardness or abrasion resistance as their prime characteristics. These coatings are usually thick by normal anodizing standards (greater than 25microns). The basic principle employed in normal anodizing and hard anodizing is same, but the later process is carried out under special anodizing conditions like: -

a. Very low temperatures.

b. High current densities.

c. Special electrolytes.

Factors that are most affecting film dissolution are the anodizing electrolyte temperature and concentration and that affecting the film growth is the anodizing current density. The production of very thick films is therefore best achieved using electrolytes with a low oxide dissolving power at low temperatures and anodizing at high current densities. These coatings find applications in the engineering industry for components, which require a very wear resistant surface such as pistons, cylinders and hydraulic gear. They are also used for electrical insulation and for achieving low friction, by impregnating the surfaces with Teflon particles. In many applications, hard anodizing is an alternative to hard chromium plating.

In micro plasmic anodizing process, a controlled high voltage AC power is applied to the aluminum part submerged in an electrolytic bath of propriety composition. Due to high voltage and high current, intense plasma is created by micro arcing at the specimen surface and this plasma in turn oxidizes the surface of the aluminum specimen. The oxide film is produced by subsurface oxidation and considerably thicker coatings can be produced.

1.7 Pretreatment before anodizing:

As no smoothing operation can be carried on an anodized sample, so surface pretreatment of the Al-substrate becomes very important before anodizing and it had a very decisive effect on the appearance and quality of a hard anodic coating. Surface pretreatment of the Al-substrate consists of two operations:

(a). Mechanical polishing: It includes operations like grinding and machining and it results in achieving a smooth, fine grained and more attractive film.

(b). Chemical polishing: The object of chemical cleaning is to remove polishing composition, dirt, oil and grease from the aluminum so as to leave a clean surface ready for the following process. It is done either in alkaline solution or acid solution. A solution of caustic soda at about 5% concentration is most widely used material for alkaline etching and it produce a clean whitish etch on aluminum. Solutions containing 10% hydrofluoric acid or a mixture of hydrofluoric acid and 2% nitric acid are widely used for acid etching. The acid etching method is widely used for special applications like production of a matt surface for lithographic plates.

1.8 Post treatment after anodizing:

Sealing is the most widely used post anodizing treatment and it means closing of the pores present in the film after the anodizing treatment. An unsealed or inadequately sealed oxide film, under certain conditions, is less resistant than a natural oxide film. Sealing can be done either in hot water, hot steam, salt solutions, water glass solutions or lacquers etc. and these processes are described as follows:

(a). Hot water sealing: Sealing in hot water is the most commonly used method and is done in hot water(distilled or dimineralized). The temperature of the hot water is between 95 to 100^0C.

(b). Hot steam sealing: It is done in hot steam. The advantage of this method is that the process is independent of the purity of available water.

(c). Bichromate solution sealing: In this method, 5 to 10% solution of sodium bichromate is used and the bichromate is incorporated into the oxide film as basic

aluminum chromate. The increased protective action of the film against certain materials is attributed to the inhibiting properties of the bichromate.

(d). Water glass sealing: In this process, oxide films saturated with a water glass solution was treated with sodium acetate or acetic acid, so that colloidal silica precipitates in the pores which were thereby closed.

(e). Nickel cobalt acetate solution sealing: This method consists of depositing the hydroxide products of the metal salts, produced during fuming off at a temperature of 90 to 100^0C, in the pores of the film as hydroxides.

1.9 REVIEW OF LITERATURE

The first work in the production of thick and hard anodic coatings for engineering applications was carried out with sulphuric acid in Russia[7] and with oxalic acid in Germany[6] and in the U.K.[8].

The sulphuric acid process has been widely adopted for hard anodizing on a commercial scale. An important consideration for its wide use is its low cost. Satisfactory hard-anodized coatings are formed on aluminum and its alloys, if the concentration of sulfuric acid is kept up to maximum of 21%(vol.). Since at concentrations above 21%(vol.), solubility of the film increases rapidly leading to decrease in film thickness and increase in porosity which results in reduction in hardness and wear resistance of the outer layers. Also, above this concentration, aluminum sulfate crystallizes out at about 13 gm/l of aluminum, so frequent electrolyte renewal is required.

The process developed by Glenn L. Martin and Co.[9] in collaborations with the Alcoa employs 15%(vol.) sulphuric acid electrolyte, operated at 2 –2.5 A/dm^2 current

density, at a temperature of 0°C. To maintain this current density, the initial voltage of 25-30V gets increased to 40-60V.

The method developed by Sanford brothers and Co.[10] in Los Angeles also operates at low temperatures (infact from 0 to −26°C) at a current density of 1.3 to 1.7 A/dm^2 and at an anodizing voltage of 15 to 60V. The electrolyte used in this process is relatively more dilute sulfuric acid(7% vol.) along with some amount of peat extract(3%), methyl alcohol(7%), nonyl alcohol(0.02%) and polyethylene glycol(0.02%).

An interesting variant of the sulphuric acid hard anodizing process is the use in Hungary[11] of very dilute solutions containing 0.5 − 2% sulfuric acid. By using dilute solutions, oxide coating of thickness 150-200 microns can be built up at 20-80V, at temperatures ranging from +5 to −5°C in an hour with higher hardness values (450 to 520 VHN) and lower porosities. Csokan and Hollo[12] produces hard coatings of thickness ranging from 100 to 250 μm in 0.1M sulfuric acid at a temperature of −1 to +1°C and at 45 − 60 volts. The hardness values were as high as 600 − 620 VHN. They have found that there is an intermediate working range of 30 to 70V for efficiently carrying the process. At voltage below 30volts, true hard films do not form and that above 70-75 volts local overheating occurs. Csokan[13] had described that at a potential around 35 volts the normal anodizing pattern obtained is of barrier layer formation followed by the uniform growth of clear porous films, but, when the voltage exceeds 35 volts the surface begins to develop small brown hemispherical spots of thick oxide which constitute primary oxidation nuclei for a second phase of growth. Rosette-shaped secondary oxide zones proceed to form around these and they spread rapidly until they merge to form a uniform coating, which is usually darker in color than the first coating.

Scott [14] also observed similar behaviour in stronger sulphuric acid solutions at concentrations up to 10% by volume.

There is evidence that, in these dilute solutions, not only the structure of' the main coating, but also the formation of the barrier layer is different than in more concentrated acid[15]. Analysis of these coatings show that they contain approximately 25% anhydrous aluminum sulphate as well as some boehmite. These coatings tends to be rougher than films produced in more concentrated acid baths. The coatings produced by this process have good corrosion resistance in the unsealed condition, particularly in warm and humid atmospheres. A disadvantage of the very dilute sulphuric acid bath is that the electrolyte may freeze on the cooling coils at low temperatures and this must be prevented by adequate circulation of coolant.

The other process, which is of commercial importance, employs oxalic acid as the electrolytic media. Black anodic coatings [10] of thickness 25-50microns with good abrasion resistance and with hardness values of 1400 VPN are reported to be obtained from a solution containing oxalic acid (50 g/l), calcium fluoride (0.1 g/l), sulphuric acid ((0.5 g/l) and chromic sulphate (1 g/l). Even though the film obtained has good abrasion resistance, the process has not been adopted so widely because the electrolyte cost is comparatively high.

With an aim to carry out the anodizing process at higher temperatures, the mixtures of two or more electrolytes have also been utilized. Lelong, Segond and Herenguel[16] have carried out anodizing by partially neutralizing the sulphuric acid bath of concentration 18%w/v by the addition of 6.65% w/v sodium hydroxide. Moreover, higher current densities in this sodium bisulphate bath have been obtained by adding

organic acids such as, citric, oxalic, tartaric or formic acid. Lelong, Segond and Herenguel[16] also use the following two electrolytes for the production of thick coatings. The first electrolyte which was a mixture of oxalic acid(80g/L) and formic acid(55g/L) results into carried out the hard anodizing process at $27^{o}C$. The second electrolyte includes mixtures of sodium bisulphate(240 g/L) and citric acid(100 g/L) and by using it this process was carried out at temperature of $30^{o}C$. When anodizing is carried out at $15^{o}C$ for 100 minutes at current densities of 60 amp/ft^2, the voltages rises from 25-60 volts in first electrolyte and 50-100 volts in second electrolyte. These processes produce smoother coatings.

Lichtenberger and Hollo[17] had investigated a formic-oxalic acid bath, which comprise of 50g/l of formic acid and 80g/l of oxalic acid. The properties of these coatings vary with the operating conditions, but at the comparatively high voltages used, up to 50 volts, barrier film thickness may be up to $540A^{0}$ and the coatings are substantially less porous(1-2 pores per cm^2) than coatings formed by other methods. The cell diameter is correspondingly larger in coatings formed in the formic-oxalic acid bath.

Shenoi, Narasimhan and Lakshminarasimhan [18] uses the mixtures of sulphuric acid and organic acid as the electrolytic bath for carrying the hard anodizing process. The organic acids employed by them are oxalic acid, tartaric acid, citric acid, malonic acid, maleic acid and formic acid. The composition of bath used by them was 6% v/v sulfuric acid + 4% w/v organic acid. The temperature employed varies from 20 to $35^{o}C$. Their result shows that thickness, hardness and coating ratio of films formed from sulfuric acid + organic acid baths is always better than films produced in plain sulfuric acid. Of the different organic acids tried, oxalic acid and tartaric acid give comparable results. Also,

addition of organic acids to the sulphuric acid improves the tolerance range of chloride ion concentration.

In one process[19],[20], it has been proposed to add to the sulfuric acid electrolyte either nitric acid or a compound producing nitrate in an amount equivalent to 1-45 g/l of HNO_3. This, it is claimed, enables anodizing to proceed to an equivalent thickness with a lower voltage, less voltage rise during anodizing, a reduction in electrical energy, less cooling and hitherto difficult alloys can be anodized more readily.

Isawa *et al.*[21] carried out hard anodizing in sulphuric acid with additions of hydrochloric acid. By adding 0.5% HCl the anodizing voltage was reduced by about 8% and with 1% HCl the voltage was reduced by about 14% while the coating ratio of the films was reduced by only 0.02 and 0.11 respectively. The same effect was obtained by additions of magnesium chloride. The economy in electrical consumption amounted to 20-30%.

The Reynolds multipurpose electrolyte[22] used for hard anodizing consists of 14 to 24%(wt.) sulphuric acid electrolyte with additions of 2-4%(vol.) of the MAE additive (2 parts glycerine to 3 parts of 70% glycolic acid) and is used at a temperature of 15-21^0C, at a current density of 2.4 to 6 A/dm^2 and an aluminum content of 4 to 8 gm/l. The high acid concentration was particularly required when anodizing for 2000 series alloy was carried out.

The all above-mentioned processes employed D.C. voltage. However, in D.C. processes there is always a possibility of burning to take place at anode, unless it is provided with efficient agitation and good electrical contacts. Also, the hard anodizing of high copper and silicon based aluminum alloys is difficult with D.C. voltage. Due to

these limitations associated with D.C. processes, hard anodizing by utilizing A.C. voltage was developed.

John, Balasubramanian and Shenoi [23], carried out A.C. anodizing(hard) of aluminum and its alloys, particularly, high copper and silicon based alloys in 10%(vol.) sulphuric acid containing 30 g/L sodium sulphate. The A.C. processes employ higher current densities effectively. The use of alternating current for hard anodizing in sulphuric acid however poses many practical difficulties like, deposition of sulphur and sulphur compounds in the pores of the oxide film during anodizing and limiting the oxide layer thickness below 12 microns without streaks and pits. These shortcomings have been overcome by the super imposition of alternating current over direct current during anodizing.

The development of hard anodizing processes using superimposed A.C. on D.C. was due to Jenny's work with oxalic acid electrolyte, which showed that the use of A.C. increased the oxide film thickness[24]. A British commercial process using this technique is known as the Hardas process and was developed by W.J.Campbell[25]. This process was carried out in electrolyte of composition 6% oxalic acid maintained at a temperature of −4°C with combined A.C. and D.C. current at a voltage of up to 60 V and current density of $5A/dm^2$.

Russian workers[26] noticed that the use of this technique improved the properties of thick coatings formed in sulfuric acid electrolyte(10% vol.) on aluminum alloys with large copper contents when anodizing was carried out at temperature range between 0 to 5°C. The value of A.C. component in these processes is primarily to raise the permissible current− density. The superimposition of A.C. often renders control of

the process easier and is also beneficial for treating alloys containing a large proportion of heavy metals.

Permaloy[27] have used a pulsed direct current for hard anodizing in a sulfuric acid-sodium lignosulphonate electrolyte .He found that pulsed currents produced harder coatings than D.C., when using a ratio of 4:1 between the higher current level (4 A/dm^2, 30sec) and the low current level (2 A/dm^2, 7.5 sec). The ratio 4:1 indicates that the higher current level is employed for four times followed by the lower current level to be applied once.

Hard anodizing can also be carried out in sulphuric acid to which salts of nickel or cobalt have been added by using interrupted or periodically reversed current[28]. Using 250-290g/l sulphuric acid with 25-30 g/l of nickel and cobalt, the current is interrupted for 4 seconds in each 20 seconds. Sulphamic acid may also be present in this process. Using sulfuric acid 50-150g/l, sulphamic acid 10-100g/l, nickel or cobalt 25-35g/l the work is made anodic for 120 seconds and cathodic for 60 seconds, this cycle being repeated.

Anodizing at low pressures i.e. at 10 mm mercury, had been attempted on a laboratory scale by Stalzer[29]. The use of low pressures prevents the accumulation of heat in the coating and also enables the use of higher current densities for short periods. He had suggested the possibilities of using this technique for hard anodizing of complex shapes as well as for basket anodizing. In order to maintain the low pressure, it is necessary to prevent hydrogen evolution at the cathode and is achieved by using a diaphragm system with the cathode compartment filled with copper sulphate solution.

The difficulty encountered in all the above mentioned process is that either they are carried out at low temperatures or if an attempt is made to carry out the process at room temperature, the properties, like hardness and wear-resistance gets hampered. Also, in hard coatings formed at low temperatures, fine failure cracks may be present when the component is withdrawn from the bath and these increases as the surface warms up after withdrawal. So, it is therefore imperative to develop electrolytic bath that can produce, at higher temperatures of 35 to 70°C the uniform oxide films with appropriate wear resistance, hardness values and desired microstructures.

So, in order to achieve this Yoshio Fukuda [30], had carried the anodizing of aluminum of 99.99% purity at high temperatures ranging from 40 to 80°C by using electrolytic baths of malonic acid, maleic acid or tartaric acid. The process had been carried out at different current densities viz. 5.67A/dm^2, 10.5A/dm^2 and 19.64A/dm^2. He found that with malonic acid, crack free and hard films of 450 to 550 VHN were obtained only below 60°C, where as, with tartaric acid and maleic acid the hardness values of 550 to 700 VHN were obtained even at temperatures of 60°C and 80°C.

Yoshio Fukuda[31], also carried out the hard anodizing of Al (99.99%) purity in a tartaric acid bath (1 mole/l.) by adding various additives . The anodizing was carried out at a current density of 1.87 A/dm^2 and at a temperature of 40°C. The effect of addition of various additives such as sulfuric acid, sodium sulfate, sulfamic acid, phosphoric acid and oxalic acid with proportions varying from 0.01 to 0.5 mole/l on the bath voltage and local corrosion of anodes and the hardness of film were examined by him. He found that, with pure tartaric acid the film was formed at 190 volts and the hardness of the film is around 585VHN. By adding 0.5 mole/l sulfuric acid, uniform film of 250 VHN was formed at

19V. With sodium sulfate and sulfamic acid, the bath voltage decreased but local corrosion took place under every condition. Adding of 0.5 mole/l of phosphoric acid forms the uniform film at a voltage of 115V, but the hardness value obtained is only 65 VHN. With oxalic acid, as an additive the hardness value of 400 VHN was achieved.

Yoshio Fukuda[32], had carried the anodizing of A6063 alloy in binary acid solutions, viz. tartaric acid, malic acid or malonic acid mixed with oxalic acid, for 20 minutes by applying a constant current density of $5.65A/dm^2$ at 40 to 60^0C. He found that final voltage was lowered by the addition of oxalic acid in baths of tartaric aid and maleic acid($105\sim135$V and $120\sim140$Vrespectively), where as in bath of malonic acid the final voltage was scarcely changed with the addition of oxalic acid. The hardness of the coating was around 300 to 470 VHN.

CHAPTER 2

EXPERIMENTAL SET UP

The amenities required for making hard anodic alumina films are mainly electrolytic cell and chemicals. These chemicals are used for electrolytic and other auxiliary purposes. The details of these are being produced below:

2.1 Electrolytic materials:

The main electrolytic materials were tartaric acid, malonic acid and maleic acid of G.R. grade and were obtained from E. Merck and Loba chemie(Mumbai, India) respectively. The oxalic acid of L.R.grade obtained from S.D.fine chemicals Ltd.(Boisar,India) was used as electrolytic modifier.

The electrolytic solutions for anodizing oxidation were prepared by dissolving weighted quantity of organic acid in water as per requirement. Since, these compounds are hygroscopic in nature, the dissolution in water is almost instantaneous.

2.2 Chemicals for other auxiliary purpose:

These includes sodium hydroxide pallets, used as the etchant for cleaning of aluminum sheet and was obtained from Ranbaxy Lab.(Punjab, India) . The chromic acid and ortho phosphoric acid were used for stripping the oxide film from anodized aluminum sheet, were of A.R. grade and were obtained from S.D. fine chem.Ltd.(Boisar, India) and Ranbaxy Lab.(Punjab, India) respectively. The mercuric acid salt, used for the amalgamation of thin oxide film, was of A.R. grade and was obtained from Glaxo Lab. (Bombay, India).

2.3 Electrolytic Cell:

The electrolytic cell consists of following main components, the electrodes, the electrolytic container, the electrical power supply, the electrolyte temperature control assembly and the magnetic stirrer. The schematic figure of the experimental set up is shown in the Figure 2.1

(i). Electrodes: The planar electrodes of dimensions (6 × 2 × 0.35 cm) were made of aluminum (anode) and stainless steel (cathode). A spacing of one cm separates them from each other.

(ii). Electrolytic container:. The electrolytic container was a cylindrical double-jacketed beaker of 300ml capacity and is made of corning glass. The internal diameter of the cylindrical beaker was 7cm and its outer diameter was 10cm with an internal depth of 8cm. The space between the double walls was utilized to circulate cool water in order to maintain the electrolyte at ambient temperature.

(iii). DC power supply: The DC power was obtained from Networks (Kanpur). It has provision for maintaining both constant voltage and constant current. The maximum rating of the equipment was:

Voltage — 0-100 Volts.

Current — 0-10 Amperes.

(iv). Magnetic stirrer : To ensure uniform temperature distribution in the electrolyte, a magnetic stirrer was employed.

2.4 Anodizing conditions:

. The details of anodizing conditions including the type of anodizing bath, its concentration, current densities, anodizing voltage range and duration of anodizing of the present study were enlisted in the table below.

Table No. 2.1   Representing the details of anodizing conditions with respect to different operating variables.

Solution type	Concentration per litre	Current Density (A/dm^2)	Voltage range (Volts)		Anodizing period(Min.)	
			S[*]	N.S.[**]	S.	N.S.
Mixture of malonic acid and oxalic acid	1.0 mole of malonic acid + 0.17 mole of oxalic acid	5.0	59 –81	53 -72	10 -60	10-70[#]
		10.0	68 –93	56-72	10-60	10-40
	2.5 mole of malonic acid + 0.17 mole of oxalic acid	5.0	68-92	—	10-60	—
		10.0	74-98	—	10-60	—
Mixture of tartaric acid and oxalic acid	1.0 mole of tartaric acid + 0.17 mole of oxalic acid	5.0	60-87	50-80	10-60	10-70
		10.0	72-96	56-84	13	10-40
	2.5 mole of tartaric acid + 0.17 mole of oxalic acid	5.0	76-96	—	10-20	—
		10.0	82-96	—	10	—
Mixture of maleic acid and oxalic acid	1.0 mole of maleic acid + 0.17 mole of oxalic acid	5.0	66-96	58-89	10-40	30-60
		10.0	72-96	60-88	10-20	20-40
	2.5 mole of maleic acid + 0.17 mole of oxalic acid	5.0	68-98	—	10-40	—
		10.0	84-96	—	10	—

*   denotes stirring.   #denotes that time-interval is 10 minutes.
** denotes non-stirring.

2.5 Procedure for anodic oxidation :

The procedure for anodic oxidation of aluminum consists of following two steps:

2.5.1   Pretreatment of aluminum sheets:

The Al-plate of chemical composition (Al -98.477%, Fe -1.16%, Si -0.334% and Cu- 0.028%) as obtained from E.P.M.A and of thickness 3.5mm was cut into rectangular pieces of cross-section approximately 6×2.0 cm. A small hole of diameter 5mm was drilled at the centre of rectangular specimen at a height of 4.5cm from the bottom.

The surfaces and edges of the specimens were first ground using an endless emery belt. After this the specimens were polished on emery papers of 0, 00, 000, 0000 grades sequentially. These polished specimens were then subjected to annealing in a vertical tubular furnace at a temperature of 300 – 350°C, for two hours. The specimens were then furnace cooled to room temperature. The main purpose of annealing is to relieve the internal stresses and to overcome any effect of work hardening. The annealed sample was then subjected to etching in sodium hydroxide solution (concentration 50-gm/l) for 2 to 3 minutes. Etching is done in order to remove any pre existing surface oxide layer. Etched sample was then rinsed in distilled water in order to remove any trace of sodium hydroxide solution sticking to the surface of aluminum sample. Rinsing is followed by air drying.

2.5.2. Anodization of aluminum sheets :

The electrodes (Al anode and stainless-steel cathode) having separation of one cm. was introduced in the double jacket electrolytic cell. The aqueous solution is

then poured in the electrolytic cell, up to a mark made on the anode, which indicates the area of anode to be immersed in electrolyte. This area depends upon the value of current density to be employed. A thermometer was then dipped in the electrolyte to measure the temperature of it. The solution was then stirred by the magnetic stirrer and also the circulation of water through the space between the outer and the inner jacket of the electrolytic container was started.

After making the connection of electrodes to power supply, the power was turned ON and then current is set. The experiments were carried out at a constant current. As the anodizing proceeds, the value of voltage raises so as to maintain this constant value of current. Anodizing time was varied from 10 to 60 minutes. Fresh additions of distilled water were done to make up for the evaporation losses taking place during the anodizing process. After anodizing, the anode was rinsed in the distilled water, followed by air-drying.

2.6 Measurements and observations:

Finally, the measurements and observations were made on the oxide coating in order to assess the physical, chemical and mechanical properties of it .The sample preparation and the procedure employed for making these measurements and observations on the oxide film were as follows:

2.6.1 Measurement of coating thickness:

The most exact determinations of thick oxide coatings are made by direct measurement under the microscope. The sample to be measured is mounted and polished as for metallographic examination, so that a cross-section of the film along with metal substrate is exposed. The thickness is then determined by observing under microscope with the help of eyepiece calibrated in micrometer. The method commonly

employed for the preparations of anodized samples for the coating thickness measurements consists of following operations:

a.) Cutting the anodized sample with diamond cutter vertically to anodized surface to expose cross-section of Al_2O_3 and support metal. Diamond cutter is employed in order to lessen the distortions, which the oxide coating may subjected during cutting process.

b.) The cut sample is then mounted on a Simplimet –2 mounting press.

c.) The mounted sample is then polished on metallographic emery paper of 00, 000 and 0000 grades sequentially.

d.) Finally, the specimen is subjected to fine polishing using a broadcloth pad on a rotating disk. Initially the rotating disk was operated at a speed of 300 r.p.m. followed by a speed of 600 r.p.m. A mixture of distilled water and alumina flour is sprayed on the cloth pad during polishing.

e.) Washing and air-drying.

2.6.2. Micro hardness Measurement:

The micro hardness values of the anodized specimens were measured with a Leitz miniload 2 micro hardness tester for Vickers hardness, having the measuring objective of magnification 500X. The indentations were carried out with an indentor having an angle of $136°$ between the opposite faces and the indentation is of square shape. The depth of penetration of the indentor is approximately the one-seventh of the diagonal of the impression. The micro-indentation tests are done on cross-sections that are in direction normal to the surface of the oxide coatings. The specimens which were

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used for the hardness measurements was prepared in the same manner as they were prepared for measurement of thickness i.e. by cutting, mounting and polishing technique.

Generally, a load of 100 grams was applied during the measurements and the thickness of each film was about 30 microns or more. At this thickness, the influence of base metal on the hardness values of the films is negligible. The load was applied for ten seconds and the diagonal of the impressions were measured with a microscope provided with an ocular screw micrometer. The hardness value was calculated from the following formula:

$$VPN = \{1.854 \times \text{load applied (in gms.)}\}/\{\text{Diagonal of impression (in microns)}\}^2$$

The impressions were taken at seven to eight places in a specimen and the mean value of corresponding diagonals was used for micro hardness calculations.

2.6.3 Determination of coating ratio :

The coating ratio is defined as the ratio of amount of coated film to the amount of consumed metal. Coating ratio was determined to measure the solvent action of electrolytes on the oxide film and also the rate of dissolution of the aluminum in the electrolyte.

Since, the hard coat is a conversion coating, it builds from the outside toward the basic metal. In other words, the coating nearest the basic metal is formed last and on the outside surface of the coating is formed first. The coating on the outside is therefore exposed to the solvent action of the electrolyte for a longer period of time and is softest The measurement of coating ratio is therefore very important parameter in hard anodizing.

As defined above, the coating ratio is calculated from the following formula:

$$\text{Coating Ratio} = (W_2-W_3)/(W_1-W_3).$$

Where, $W1$ = Weight of the sample before anodizing.

W_2 = Weight of the sample after anodizing.

W_3 = Weight of the sample after dissolving the coating.

The dissolution of alumina coatings were carried out in a aqueous solution consisting of mixture of phosphoric acid and chromic acid and its concentration was:

Phosphoric acid ---- 35 ml/L

Chromic acid (AR grade) ---- 20 gm/L.

This solution dissolves only the oxide coating and does not affect the aluminum metal and depending upon the thickness the oxide coating it takes one to ten minutes to strip. The dissolution of coating takes place at a solution temperature of $98-100^{\circ}C$. This temperature range of the solution was maintained by placing a beaker containing the solution over a heating element and this heating element was connected to the ON/OFF relay unit through variac. Utilization of variac prevents the breakdown of heating element.

2.6.4 Determination of specific conductivity:

The conductivity of electrolytic solutions were determined by using conductivity cell of type : CD – 06. This cell has platinum electrodes of cross-section 0.5 × 0.5cm with a separation of 0.5 cm. This cell is electrically connected to the Systronics

Digital Direct Reading Conductivity Meter. The main advantage of this meter is that it enables to measure the conductivity, without manual balancing and the specific conductivity is read directly on a digital panel. This instrument incorporates an integrated circuitry and thus the power consumption is kept very low. The conductivity range of the meter is 0 – 200 m MHO in 5 ranges, with a measuring accuracy of ±1%.

Measurement of specific conductivity involves following steps :

(a.) After switching on the meter, the CAL/READ switch is put on CAL position and the CAL control is adjusted to full scale reading on the digital panel (199 m MHO).

(b.) The conductivity cell is then immersed in standard solution, the specific conductivity of which is accurately known at the temperature of solution.

(c.) Now, the CAL / READ switch is put in READ position and range switch is turned to get the reading in the range corresponding to conductivity of standard solution and adjusted to get its actual value on panel meter by adjusting the CELL CONSTANT.

(d.) The cell is then dipped in the distilled water to remove any trace of standard solution sticking to it.

(e.) To get the specific conductivity of the electrolytic solution, the cell is then dipped in the solution and the reading is noted from the digital panel.

2.6.5 Electron microscopic observation:

In the present study, the microstructures of the anodized sample were observed by transmission electron microscope at an accelerating voltage of 120 KV. This becomes necessary because of the extreme fineness of microstructures of the oxide coating. Sample for the transmission electron microscope was made on a thin foil of

aluminum of purity 99.99%. The care was taken to anodize only one flat surface of the foil. As a result, the opposite flat surface and the edges of the foil were protected from anodic oxidation by applying usual nail polish. The samples were anodized only after nail polish gets self-dried. Rinsing in distilled water follows anodic oxidation of aluminum foil. The nail polish from the foil was removed by dissolution in acetone through cotton swabbing. Then the marking of squares of dimension (3×3mm) was made on the foil and the entire specimen was subjected to amalgamation in mercuric chloride solution. Care was taken to contact the foil with the mercuric chloride solution from aluminum(unanodized) side. Amalgamation was allowed to continue until the squares of oxide film separates from each other and starts floating on the mercuric chloride solution surface. The oxide squares were further washed in distilled water and then picked up on the electron microscope grids, followed by drying subsequently.
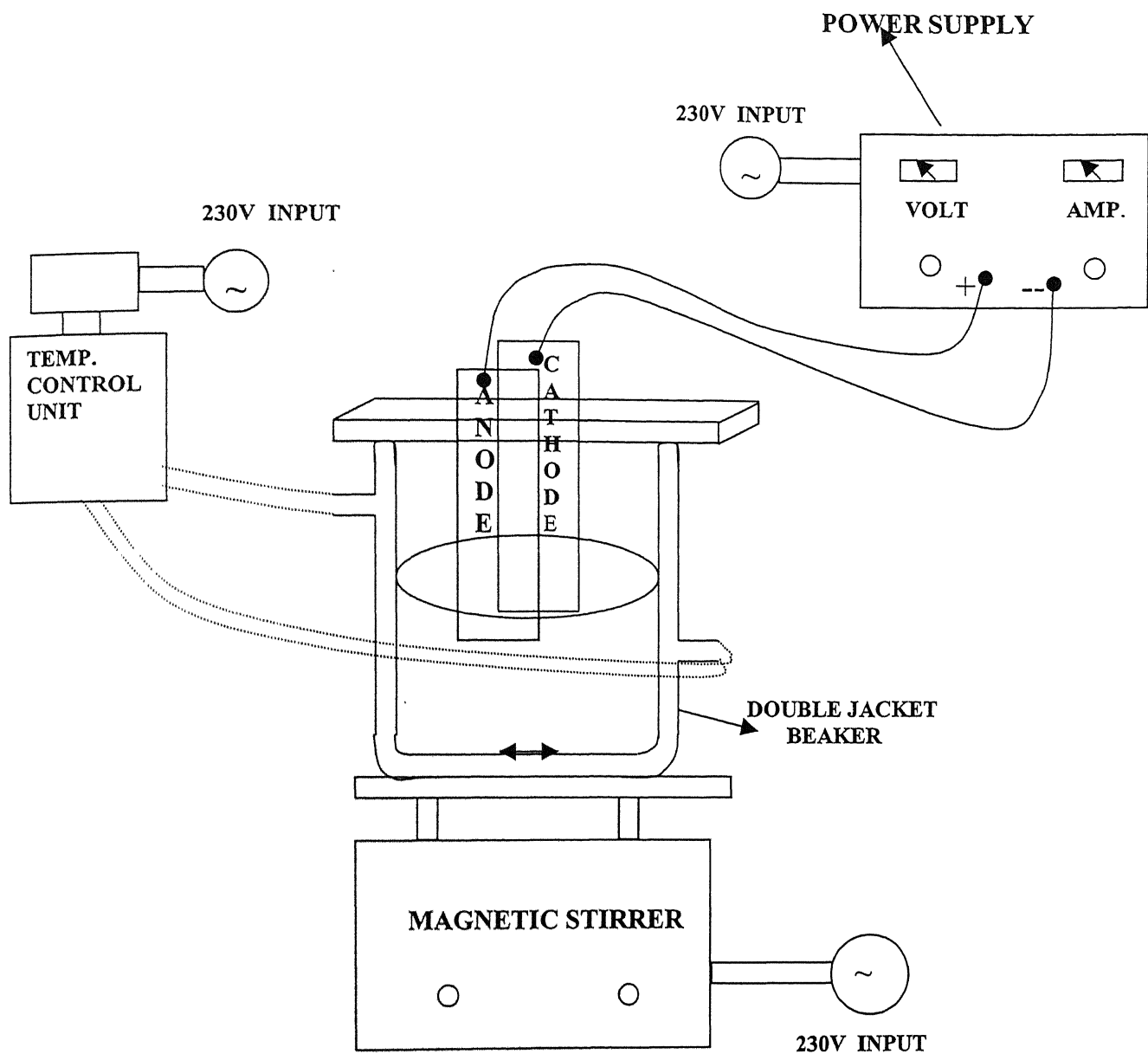
Figure 2.1. Schematic diagram of the experimental set-up used in the present study.

CHAPTER 3

Results and Discussions

This chapter gives the effect of various operating variables like different electrolytes, current densities and stirring conditions on the physical, chemical and structural aspects of oxide coatings.

3.1 Physical appearance of oxide coating:

The oxide films produced by hard anodizing treatment were uniform, integrally colored and free from cracks. The color of the anodic films produced in malonic acid + oxalic acid was brown and whereas sandstone color was produced in maleic acid + oxalic acid and tartaric acid + oxalic acid (Figure 3.1). It has been observed that color of the film becomes increasingly deeper with increase in current density and anodizing time.

Burning effect was specifically observed in case of high concentration electrolyte and many times it become so pronounced that anodic oxide film got separated, due to mismatch in thermal expansion(oxide coating and aluminum metal) from aluminum substrate when stirring was not carried out during anodic process..

3.2 Electron microscopic observations:

The structural features of the porous oxide coating investigated with the electron microscope shows that this coating consists of close packed cells of oxide, predominately hexagonal in shape. Each hexagonal shape contains a single pore and is shown in the

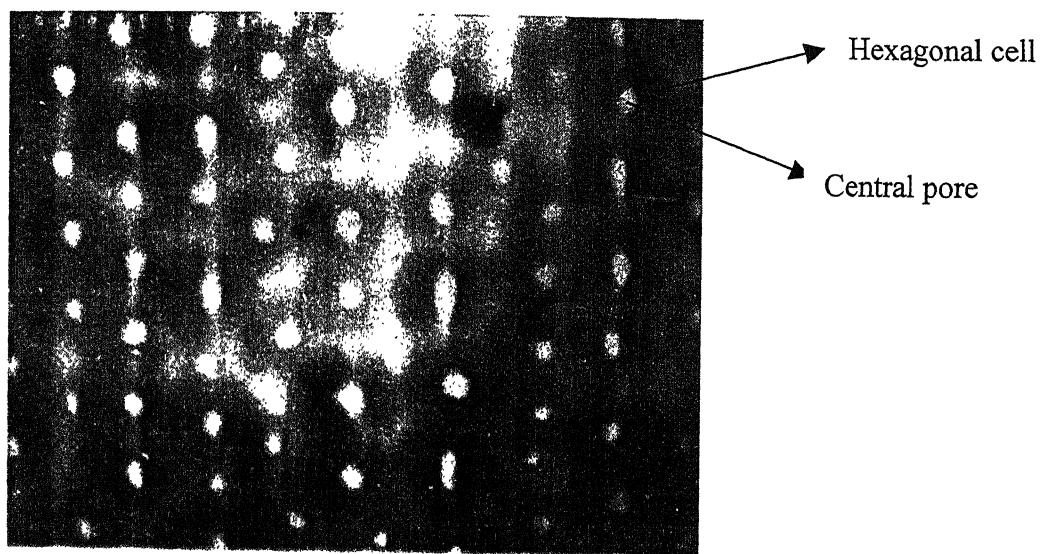Figure 3.2 and Figure 3.3:. This structure had been noticed with inorganic electrolytes, by other workers[33].

Figure 3.2 Structure for mixture of malonic acid and oxalic acid at 75 V, anodized for ½ min. Electron micrograph (50,000X)

Pore diameter in mixture of malonic acid and oxalic acid electrolyte is more as compared to other electrolytes used in present study, so, this mixture seems to be decisively more corrosive than other organic mixtures used, as easiest approach for the corrosive media is through the pores of coating[4]. The results showing comparison of pore diameter and cell size between different organic mixtures used are presented in Table 3.1 and from Figure 3.2 to Figure 3.4. In case of bath consisting of Tartaric acid and oxalic acid, the pore diameter is smaller than bath consisting of Maleic acid and oxalic acid, as well the cell size. Table 3.1 also shows the pore volume (volume of pores per unit square area per unit thickness) and it is found that even though the pore diameter

of the anodic film produced in Tartaric acid + oxalic acid bath is less than that of oxide film produced in Maleic acid + oxalic acid bath, the pore volume is more. It shows that the corrosive nature of the bath consisting Tartaric acid + oxalic acid is more than Maleic acid + oxalic acid bath.
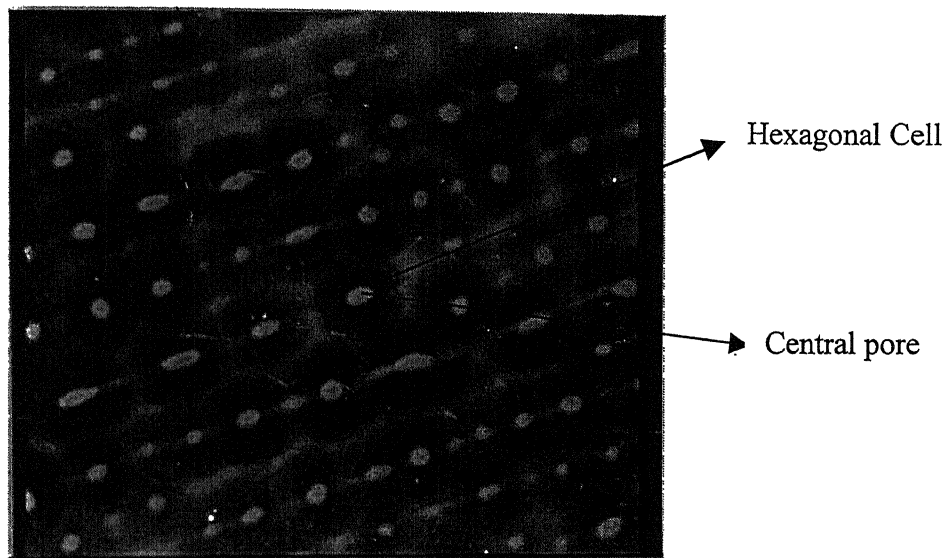

Figure 3.3 Structure for mixture of maleic acid andoxalic acid at 75 V, anodized for ½ min . Electron micrograph. (50,000X).
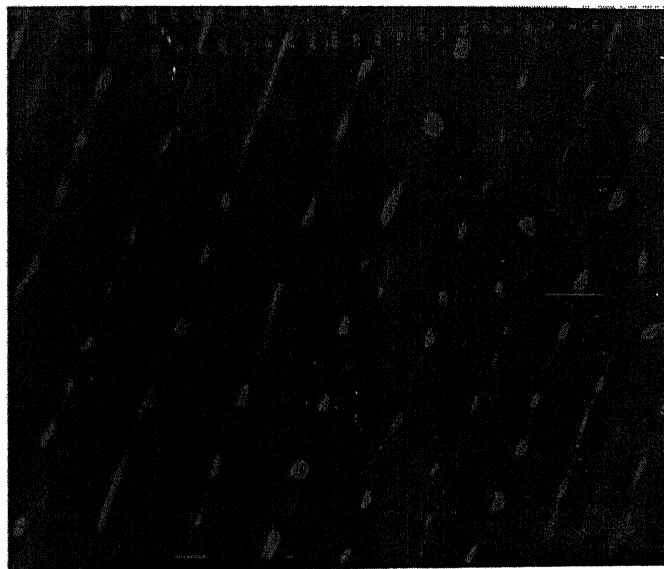

Figure 3.4 Structure for mixture of tartaric acid and oxalic acid at 75 V anodized for ½ min . Electron micrograph(50,000X)

With increase in forming voltage, the cell size increases and this variation is shown in case of mixture of malonic acid and oxalic acid from Figure 3.5 to Figure 3.7. Similar results had also been noticed with inorganic electrolytes[4]

Figure 3.5   Structure for mixture of malonic acid and oxalic acid at 60V, anodized for ½ min. Electron micrograph.(100,000X)
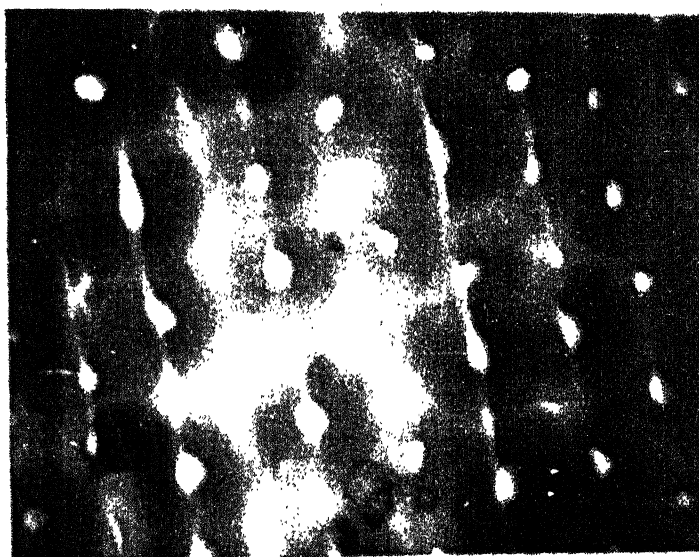

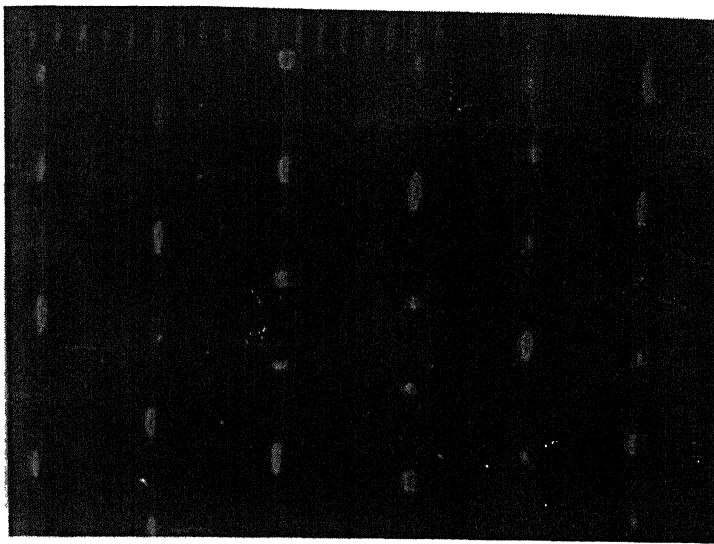**Figure 3.6**   Structure for mixture of malonic acid and oxalic acid at 75 V, anodized for ½ min. Electron micrograph.(100,000X)

Figure 3.7 Structure for mixture of malonic acid and oxalic acid at 90 V, anodized for ½ min. Electron micrograph (100,000X)

The aluminum foils exhibit parallel slip lines as a result of rolling. The disposition of pores are therefore seems to be controlled by the stress field of slip lines as a result the pore are crowded along the slip line and, so, maximum density is along the slip line in comparison to any other direction. This is evident from Figure 3.2 to 3.7. The linear pore density obtained from Figure 3.4 along the slip direction (AB) is 0.24/cm and along other direction (AC) is 0.135/cm.

Figure 3.8 shows that heat treatment of oxide film at 500^0C for one hour, seems to induce shrinkage in the film and relieved the local stresses resulting to leading to higher surface pore density than virgin oxide and also in disappearance of cells.

Figure 3.9 shows the electron diffraction pattern for oxide coating formed in malonic acid + oxalic acid bath. Only two broad rings are observed. This is unlike the structure of poly-crystalline material. The inter planar spacing values of the ring are $6.035A^0$ and $3.923A^0$ respectively. This values does not correspond to inter planar

spacing values of crystalline alumina, leading to conclude that structure is amorphous in nature[34],[37],[38]. Similar results were also observed in other electrolytic baths used.
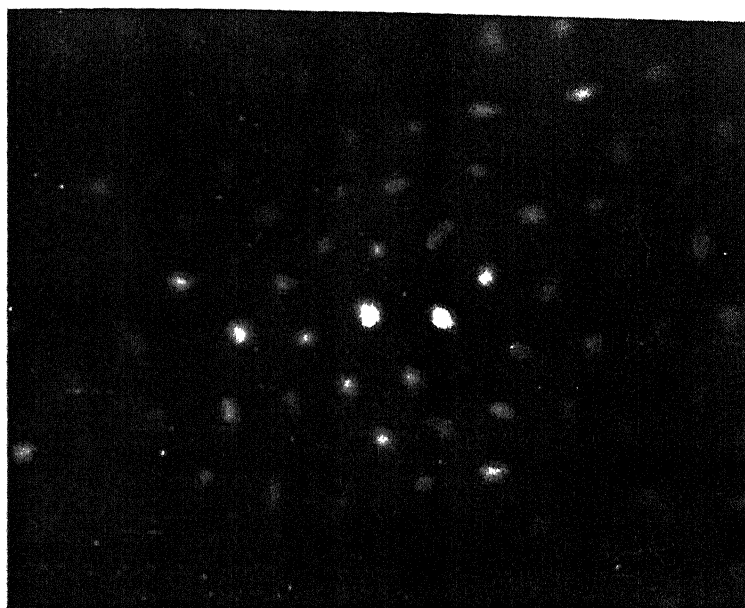

Figure 3.8 Structure for mixture of malonic acid and oxalic acid anodized for1/2min. at 75 V. Film is heat treated for one hour at 500^{0}C. Electron micrograph (50,000X)

Figure 3.9 Electron Diffraction of alumina formed in mixture of malonic acid and oxalic acid

3.3 Bath voltage studies:

Depending upon chemistry and composition of different electrolytes, the anodic oxidation of aluminum starts at a characteristic(of an electrolyte) voltage. When cell approaches this value of voltage(at any fixed current density), anodizaton starts. However the formation of pores due to corrosive action of the electrolyte will offer the bath solution to be in contact with the virgin material and the oxide layer will grow. Due to this increasing oxide coating thickness the resistance offered by the oxide coating will increase and it will lead to increase in voltage with increase in anodizing time. This increase in voltage saturates after some time termed as stationary or critical voltage. Further progress of anodization proceed at this voltage with minor changes(+2 to +3%). It has been found that the stationary voltage for the malonic acid was below 100 volts where as in tartaric acid or maleic acid it was around 170 volts[30]. This critical voltage had been found to get reduced due to additions of small amount of oxalic acid as a result of increase in conductivity of the bath[32]. This behavior had been examined for electrolytes like mixture of tartaric acid, maleic acid or malonic acid and oxalic acid, for different current densities and stirring conditions and the result of the present study is presented graphically from Figure 3.10 to Figure 3.12.

The voltage vs. time profile for different electrolytes is shown in Figure 3.10 and it is noted that critical voltage for mixture of maleic acid and oxalic acid was greater than other electrolytic bath used.

It is observed that with increase in the values of current density the forming voltage also increases and is represented graphically in Figure 3.11. This is because with increase in current density the rate of growth is more[35] and as oxide coating is non

conducting in nature, the resistance to the passage of current increases with increases in thickness and hence voltage requirement is more.

Figure 3.12 shows that under stirring conditions, the bath voltage is found to be more as compared to anodizing under non- stirring conditions. This behavior is also observed by Henley[36] . In unstirred conditions, the temperature generated is high in the bath, there by reducing the resistance. As increase in temperature is expected to enhance the chemical dissolution along the pore walls resulting in decrease in oxide film thickness. Whereas in case of stirred condition, the convective heat transfer(forced) will lead to uniform and lesser bath temperature leading to increase in voltage.

3.4 Coating ratio studies:

The variation of coating ratio (amount of coated film to the amount of metal consumed) for operating variables like different solutions and concentrations, anodizing time and stirring conditions is shown in Table 3.2.

The coating ratio is influenced by treatment time[23] and this relationship is represented in the Table 3.2. The decrease in value of coating ratio is taking place with time at constant current density. This is because the voltage rises as the coating thickness increases and this reflects increasing dissolution of the coating during its growth associated both with a larger active surface area with progressive dissolution in the pores and with increase in local temperature due to higher voltage required as the coating grows in thickness. The bath comprising of malonic acid + oxalic acid had the lowest coating ratio amongst all bath used which indicates the highly corrosive nature of it(amongst all) and is evident from electron microscopic studies(Table 3.1).

It is also evident from Table 3.2 that with increase in current density the coating ratio also increases. This is attributed to a decrease in dissolution rate with in the pore channel because of build up of solution. Increase in coating ratio at higher current density is inevitably associated with a steeply rising voltage with time

As evident from the Table 3.2, it is noticed that with increase in concentration of base acid of the bath at fixed current density the coating ratio values also increases This is because that the rate of film formation is larger at higher concentrations than anodizing at low concentrations which also means lower amount of dissolution.

The coating ratio values under stirring conditions were found more as compared to anodizing under non-stirring conditions and are represented in the Table 3.3. This is attributed to the effective heat transfer under stirring conditions, hence lower is the dissolution rate.

3.5 Coating thickness studies:

Study was conducted for measuring the coating thickness with respect to anodizing time for various operating variables like current density, type of electrolytic solutions and stirring conditions. It is found that coating thickness is an increasing linear function of anodizing time and this behavior is evident from Figure 3.13 to Figure 3.15

Figure 3.13 shows the variation of oxide film thickness with time for various electrolytes used at $5A/dm^2$. It is seen that the electrolyte that is a mixture of maleic acid and oxalic acid produced the highest coating thickness for the same anodizing time as compared to other electrolytes. The conductivity of the electrolytes is shown in Table 3.4 as measured in the lab. It is interesting to note that this electrolyte, which produces higher

thickness, has also the highest conductivity amongst all. This electrolyte also exhibit highest coating ratio in the present study indicating the least dissolving tendency which is attributed to less corrosive nature of Maleic acid and oxalic acid bath as compared to other baths. The coating ratio values are shown in the Table 3.2.

Figure 3.14 shows variation of coating thickness with time for two different current densities namely $5A/dm^2$ and $10A/dm^2$. It is clear from this behavior that higher current densities produced higher oxide thickness at each point of time, as rate of growth is higher for higher current densities[35].

Figure 3.15 shows the variation of coating thickness with time for mixture of malonic acid and oxalic acid bath at a current density of $5A/dm^2$ for stirring conditions. The coating thickness under stirring conditions was found to be greater as compared to thickness under non-stirring conditions. This is accounted by the facts that stirring of the electrolyte increases the electrode-reaction rates, which are diffusion controlled. Stirring also avoids the stagnation of solution and also facilitates in dispersion of electrode reaction products.

3.6 Micro-hardness studies:

Micro hardness measurements on the oxide deposit indicates that oxide coating has higher hardness as compared to that of the base metal(aluminum). The oxide coating developed in the present studies has hardness values in the range of 375 to 475 VHN where as that of the substrate metal is around 28 –32VHN. Yoshio Fukuda[32] had found these values within range of 300 to 450 VHN conducted at 40-60°C, which is close to present finding carried at room temperatures. The result of study of micro

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hardness with processing conditions such as current density, electrolyte type/concentration and stirring operations are present in Table 3.5.

As seen from the Table 3.5 all of the organic acid electrolytes under present study give rise to high hardness at room temperature (30^0C) anodizing due to their less corrosive nature leading to smaller pore size. In addition, high forming(anodizing) voltage of these electrolytes resulted in larger pore separation leading to higher resistance against abrasion. This is unlike inorganic electrolytes where very low temperatures($<5^0$C) of anodizing is maintained to obtain such values of micro hardness. There seems to be some mathematical relationship between pore diameter, cell size and micro hardness values. But, due to lack of data available this relationship cannot be deduced. Further experimental studies and mathematical modeling is required to find this relationship.

Hardness values generally increases with current density. However, as per our experimental results(Table 3.5), the increase in hardness with current density was not well recognized in mixture of maleic acid and oxalic acid bath and it was also not so large in other baths. Since, the oxidation reaction is exothermic in nature, so an enormous amount of heat is produced due to high forming voltages of these baths. Hence, the temperature near the anode rises markedly, which increases the oxide dissolution rate and therefore, the increase in hardness values with current density is not quite significant.

It is also evident from the Table 3.5 that the specimens anodized under stirring conditions had high hardness values as compared to specimens anodized under non-stirring conditions. This is because the uniform stirring results in effectively removal of

heat from the electrode-electrolyte interface, which in turn reduces the oxide dissolution rate and hence coating of higher hardness can be achieved.

Figure 3.16 show that increasing the malonic acid concentrations from 1.0mole/l to 2.5mole/l in a bath comprising of a mixture of malonic acid and oxalic acid results in increasing the micro hardness values, but, almost approaching a saturation point at higher concentrations(1.75mole/l and 2.5mole/l). This may be due to decrease in porosity at higher concentrations. This increase is also evident at different current densities. During this study, the concentration of oxalic acid was remained fixed at 0.17mole/l.

3.7 Comparative studies:

The object of the present studies is to see the possibility of anodising the aluminium with maximising the hardness, coating ratio and coating thickness by minimising the voltage at room temperatures.

In our experiments, magnetic stirring and outer circulation of water was carried out to reduce the effect of exothermic heat generated during the process. The upper voltage limit during the process was kept at 100V, considering the economics of the process.

The obtained maximum hardness as per literature is 550~700 VHN using Tartaric acid bath and Maleic acid bath with 170-190 V at 60°C and the hardness values obtained using oxalic acid as an additive in these baths were 300 to 450 VHN at 40-50°C with 105~135V and 120~140V respectively. The current density employed by them was 5.67A/dm². The present studies show that at room temperature (30°C), it is possible to achieve a maximum hardness of 400-480 VHN with Maleic acid(1 moles/l) and oxalic

acid bath at 5A/dm^2, 68-96V and 370-470VHN with Tartaric acid(1 moles/l) and oxalic acid bath at 5A/dm^2, 60-87V : Also, 420-480 VHN of hardness was achieved using Malonic acid(2.5moles/l) and oxalic acid bath at 5A/dm^2, 76-98V.

Maximun thickness obtained in the present studies is 70 microns with Malonic acid and oxalic acid bath at 10A/dm^2, 68-93 V for 1 hour. However, the hardness and coating ratio achieved in this electrolyte is found to be less as compared to other baths used.

Maximum coating ratio combined with maximum hardness is obtained with bath consisting of Maleic(1 mole/l) and Oxalic Acid, but, maximum thickness is not achieved in this bath.

It is also found that voltage of 68-97 V (5A/dm2) against the 120-140V (5.65 A/dm2) [32] is measured for achieving the hardness of ~450 VHN in the present studies. However in the present studies Al metal of commercial grade is used whereas in the later Alluminium 6063 alloy was used.

Table 3.1 Comparison of pore diameter, cell size and pore volume in different anodizing solutions.

S. No.	Anodizing solution (moles/litre)	Pore diameter(P) ± 10% (Armstrong)	Cell size(C) ± 10%. (Armstrong)	Pore Volume(V) $V= 78.4*(P^2/C^2)$
1.	Malonic acid (1mole/l) + Oxalic acid (0.17 mole/l)	212	650	8.35%
2.	Tartaric acid (1mole/l) + Oxalic acid (0.17 mole/l)	162	612	5.60%
3.	Maleic acid (1mole/l) + Oxalic acid (0.17 mole/l)	175	650	5.37%

Table 3.2 Coating ratio in different anodizing solutions for different anodizing time at different current densities and concentrations.

S. No.	Concentration per litre	Current Density (A/dm^2)	Coating Ratio — Anodizing time(minutes)						Mean coating Ratio
			10	20	30	40	50	60	
1	Malonic acid (1.0 mole) + Oxalic acid (0.17 mole)	5.0	—	1.40	1.35	1.32	1.29	1.26	1.324
		10.0	1.42	1.41	1.39	1.40	1.38	—	1.40
	Malonic acid (2.5 mole) + Oxalic acid (0.17 mole)	5.0	1.49	1.48	1.46	1.43	1.42	1.39	1.446
		10.0	1.51	1.46	1.46	1.44	—	1.41	1.456
2	Tartaric acid (1.0 mole) + Oxalic acid (0.17 mole)	5.0	—	1.38	1.36	1.35	1.35	1.33	1.354
		10.0	1.46	—	—	—	—	—	1.46*
	Tartaric acid (2.5 mole) + Oxalic acid (0.17 mole)	5.0	1.54	1.52	—	—	—	—	1.53
		10.0	1.62	—	—	—	—	—	1.62*
3	Maleic acid (1.0 mole) + Oxalic acid (0.17 mole)	5.0	1.46	1.45	1.43	1.42	—	—	1.44
		10.0	1.48	1.46	—	—	—	—	1.47
	Maleic acid (2.5 mole) + Oxalic acid (0.17 mole)	5.0	1.51	1.48	1.49	1.48	—	—	1.49
		10.0	1.64	—	—	—	—	—	1.64*

* Anodizing time was set at 10 minutes because of experimental limitation.

Table 3.3 Coating ratio for stirring conditions in bath comprising of Maleic acid(1 mole/l) and oxalic acid(0.17 mole/l)

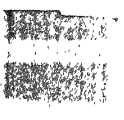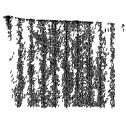| S.No.	Concentration (moles/litre)	Anodizing time (Minutes)	Coating ratio	
			Stirring	Non-stirring
1.	1.0mole of maleic acid+ 0.17 mole of oxalic acid	10	1.46	1.35
2.	1.0 mole of maleic acid+ 0.17 mole of oxalic acid	50	1.41	1.29

Table 3.4 Effect of addition of oxalic acid on conductivity of Malonic, Tartaric and Maleic acids at 26^0C

S. No	Varying concentrations of oxalic acid. (moles/litre)	Conductivity(m MHO/cm) at $26\ ^0$C.					
		Malonic Acid (moles/litre)		Tartaric Acid (moles/litre)		Maleic Acid (moles/litre)	
		1.00 (moles/l)	2.50 (moles/l)	1.00 (moles/l)	2.50 (moles/l)	1.00 (moles/l)	2.50 (moles/l)
1.	0 .0	13.02	14.63	10.04	10.30	38.20	40.30
2.	0.10	24.70	21.00	19.10	14.60	44.10	42.30
3.	0.15	28.80	23.50	23.00	18.51	49.10	45.60
4.	0.20	32.70	26.40	26.30	21.40	54.00	49.30
5.	0.30	39.30	30.60	33.20	24.70	58.60	54.20
6.	0.40	44.90	34.60	38.80	—	—	—

Table 3.5 Comparison of Micro-hardness of andized coatings in different anodizing solutions at different current densities and stirring conditions

S. No.	Anodizing solutions	Micro-hardness (VHN)			
		Current-density (5 A/dm^2)		Current density (10 A/dm^2)	
		Stirring	Non -stirring	Stirring	Non-stirring
1.	Malonic Acid (1.0 m/l*) + oxalic acid (0.17 m/l*)	430	390	445	375
2.	Tartaric Acid (1.0 m/l) +oxalic acid(0.17 m/l)	465	440	——	430
3.	Maleic Acid (1.0 m/l) +Oxalic acid (0.17m/l)	480	460	485	430

* m/l stands for moles/litre

anodizing time (minutes)	10.0	30.0	40.0	30.0
Current density (A/dm²)	5.0	5.0	5.0	10.0
Malonic Acid(1.0m/l*) + OxalicAcid(0.17m/l)				
Tartaric Acid(1.0 m/l*) + Oxalic Acid(0.17m/l)				
Maleic Acid(1.0 m/l*) + Oxalic Acid(0.17 m/l)				

* m/l stands for moles/litre.

Figure 3.1 Photographs of oxide coatings showing colors and appearance at different anodizing tir and current densities..
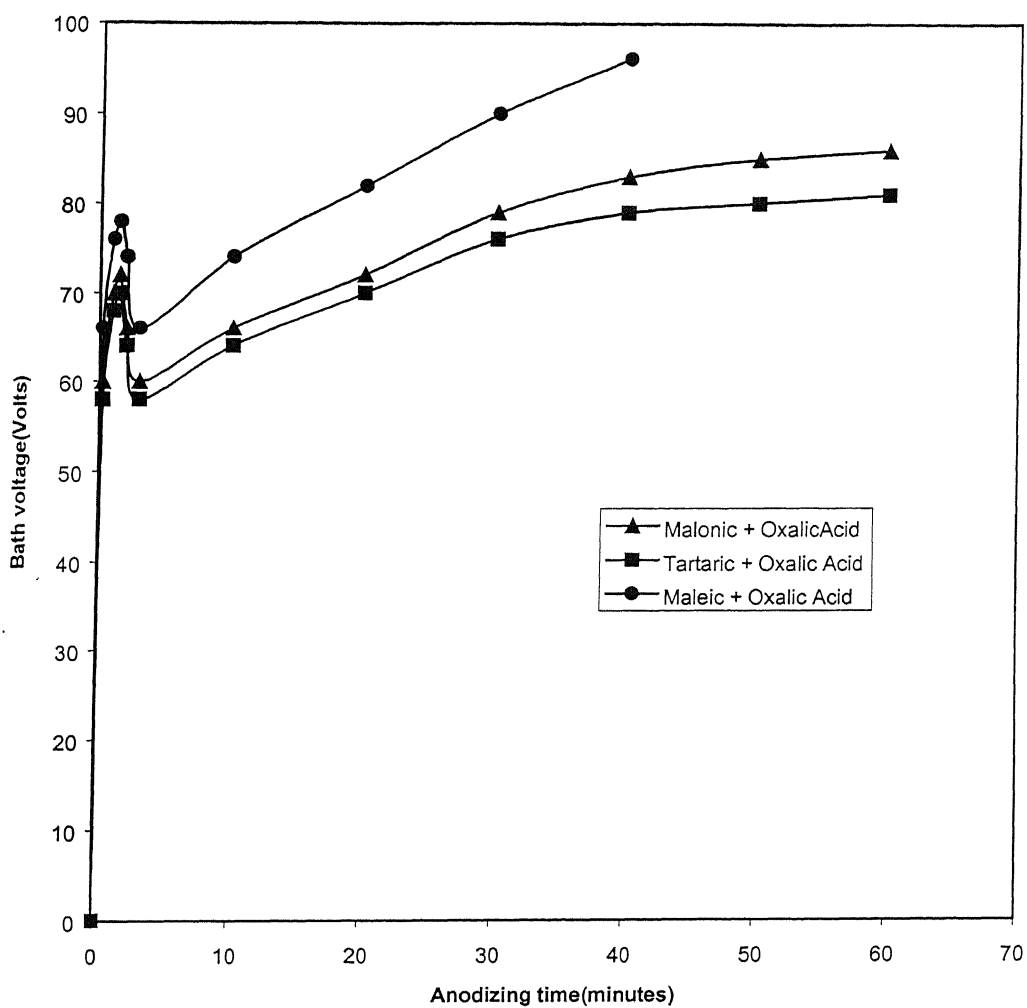
Figure 3.10 Effect of anodizing time on bath voltage in different anodizing solutions at 5A/dm^2.
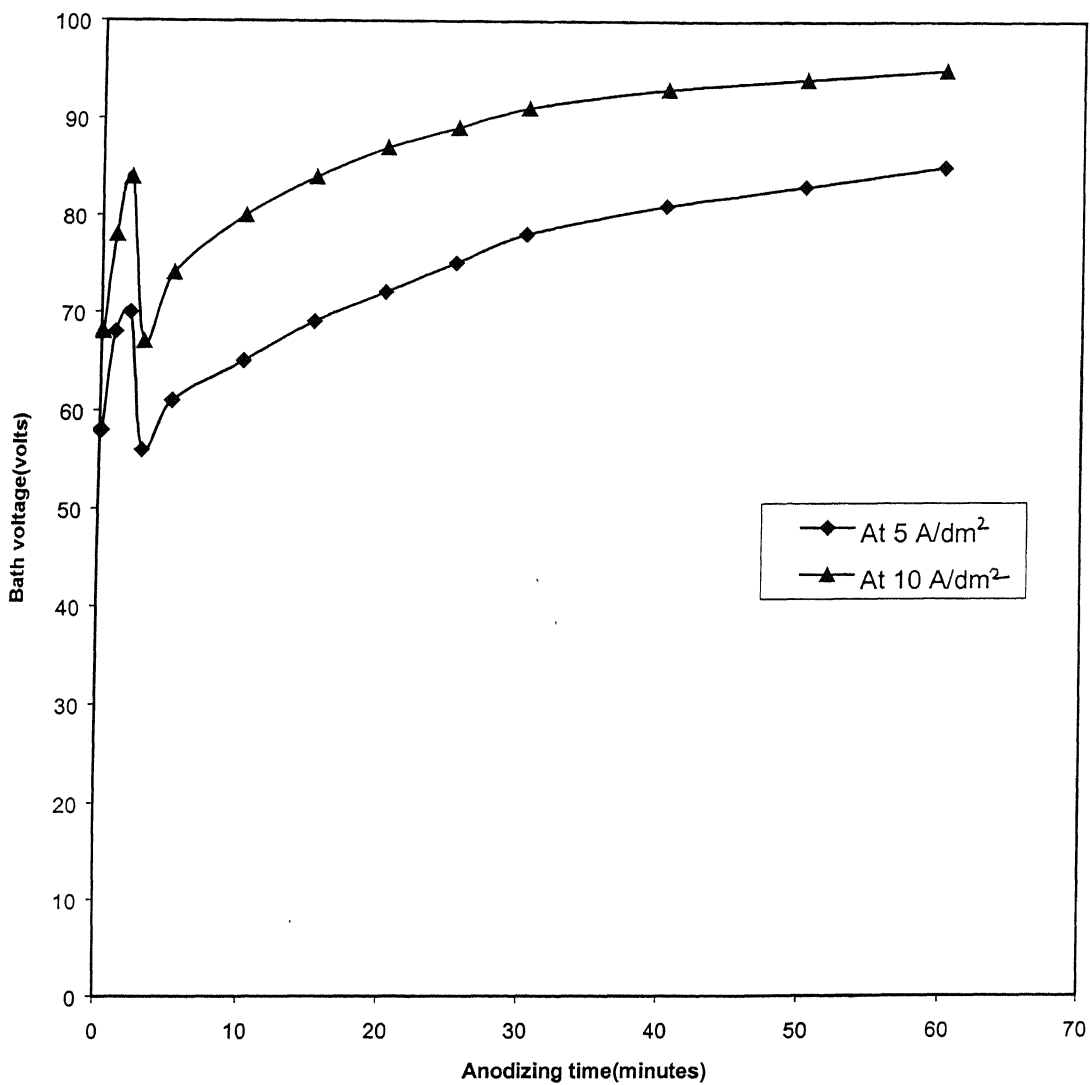
Figure 3.11 Effect of anodizing time on bath voltage time at different current densities in mixture of malonic acid (1.0 m/l) and oxalic acid (0.17 m/l) solution.
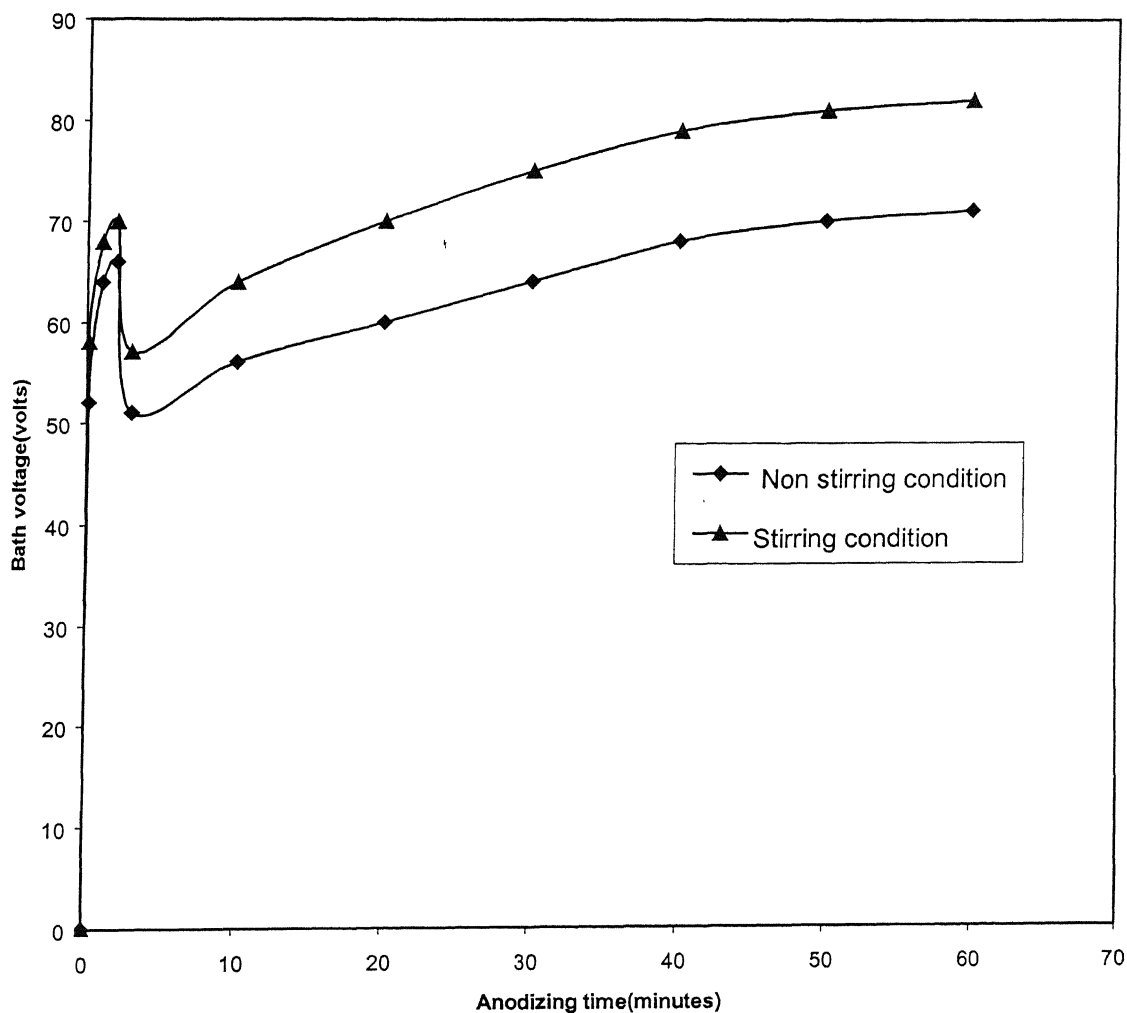
Figure 3.12 Effect of anodizing time on bath voltage under stirring conditions in mixture of malonic acid (1.0 m/l) + oxalic acid (0.17 m/l) solution at 5A/dm^2.
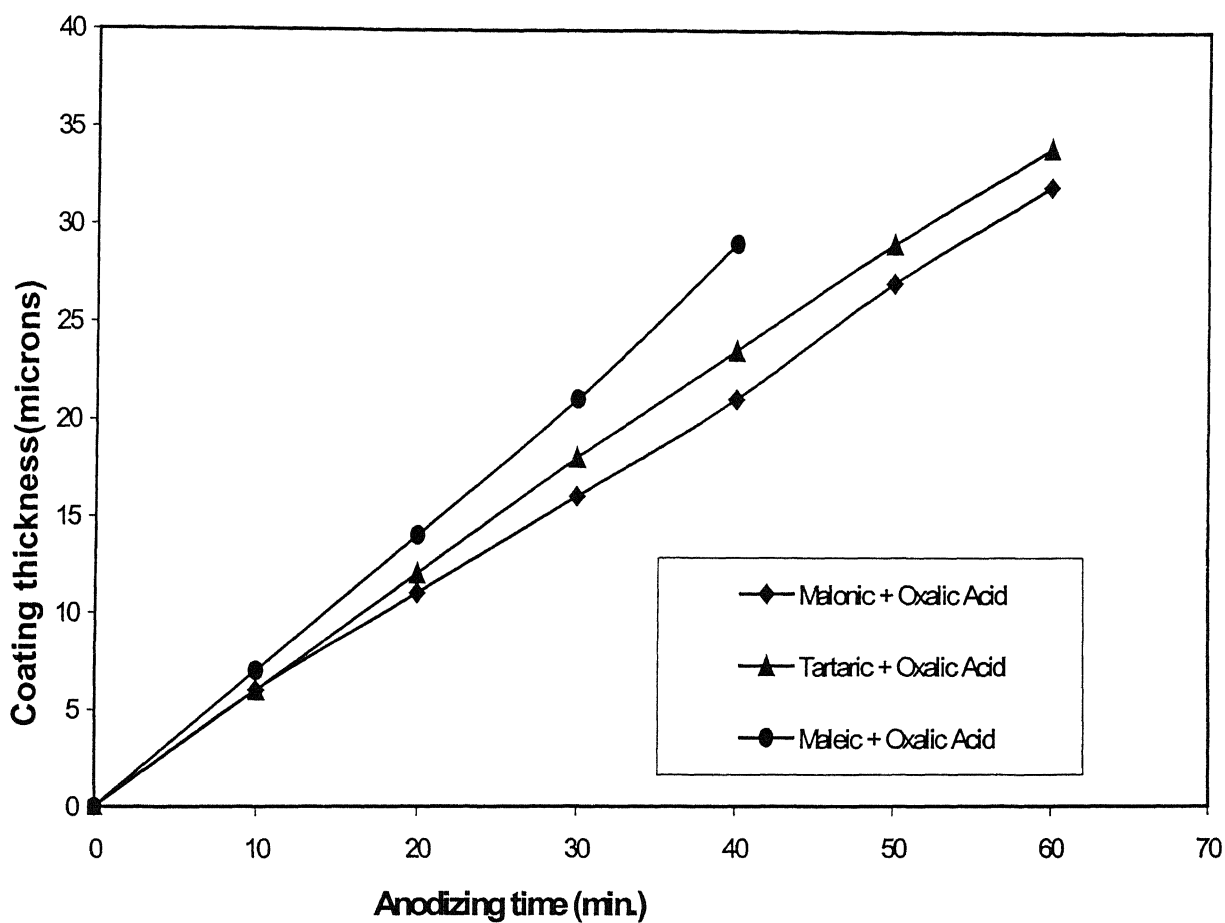
Figure 3.13   Variation between coating thickness and anodizing time in different anodizing solutions at 5 A/dm^2..
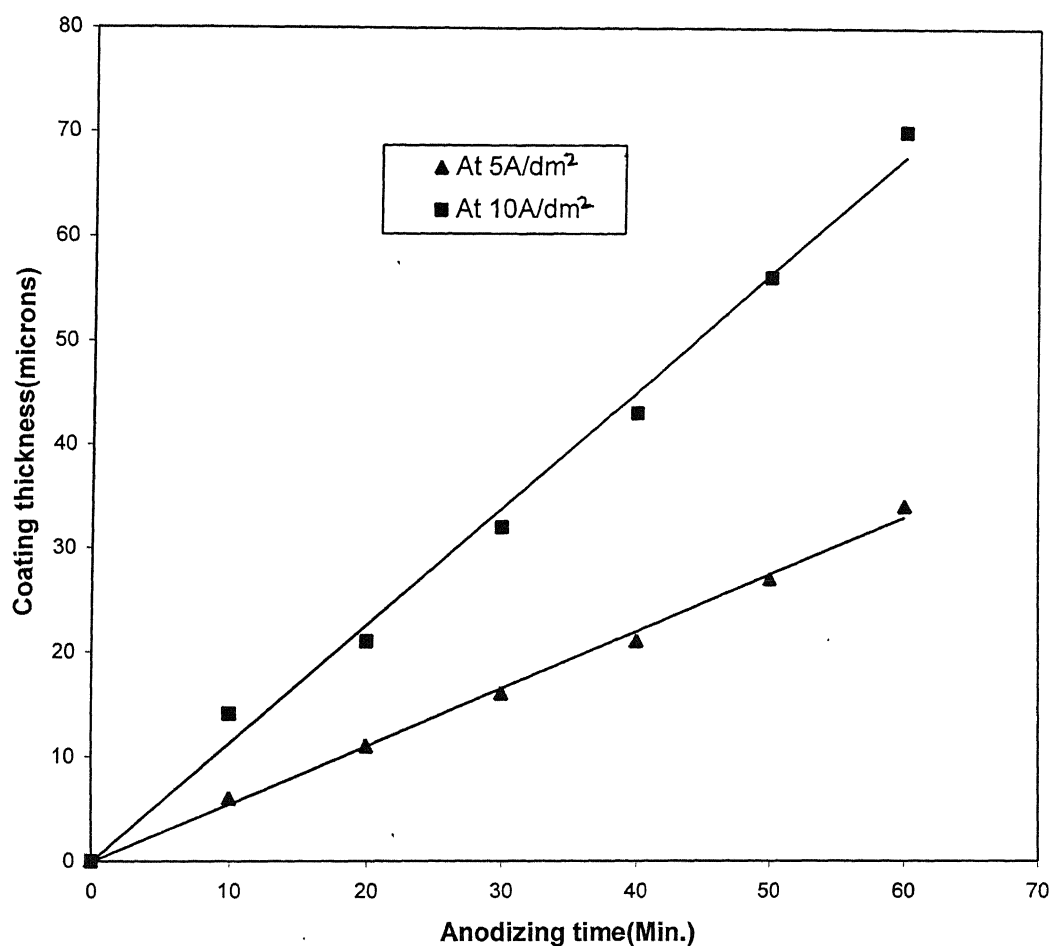
Figure 3.14 Variation between coating thickness and anodizing time under different current densities for mixture of malonic acid (1.0 m/l) + oxalic acid (0.17 m/l) solution.
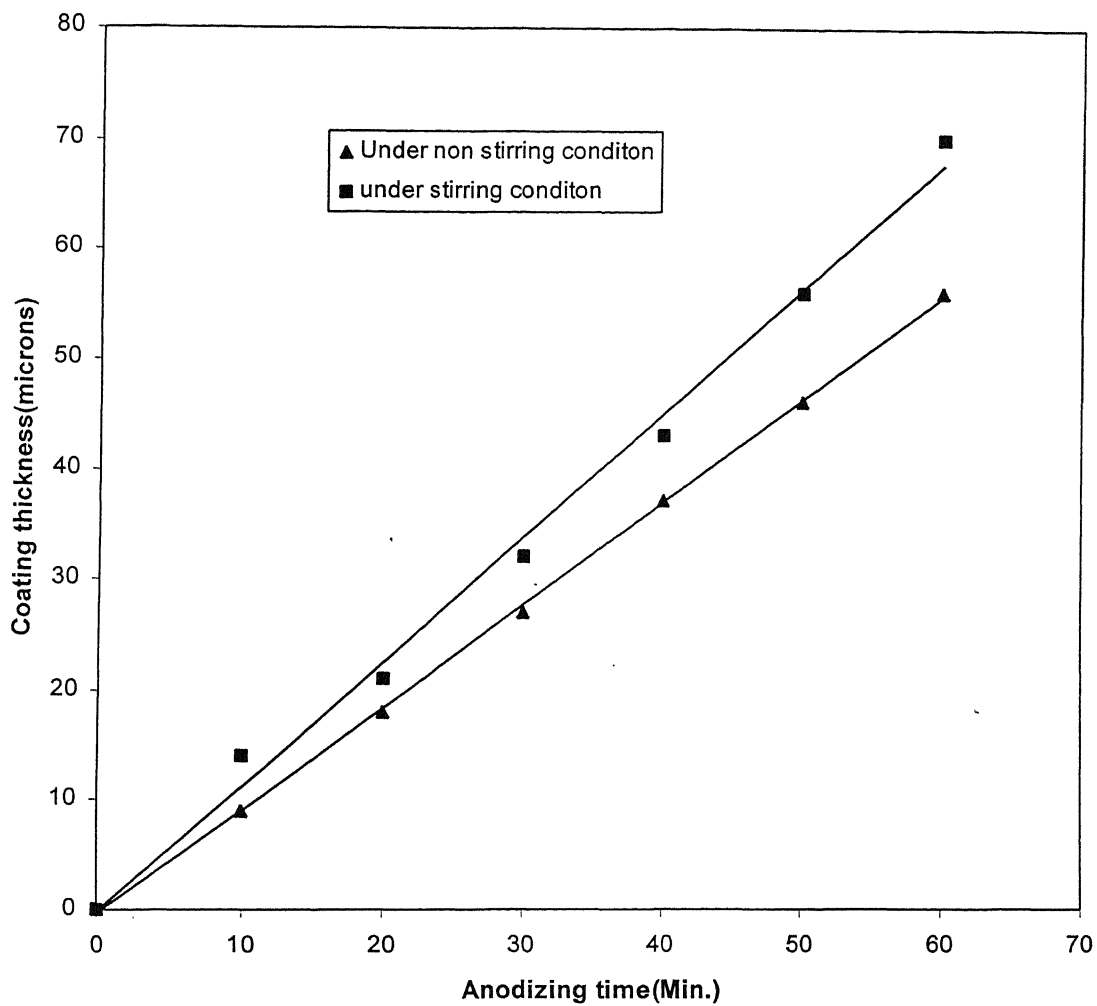
Figure 3.15 Variation between coating thickness and anodizing under stirring and non- stirring conditions for malonic acid(1.0m/l) + oxalic acid (0.17m/l) solution at 10 A/dm^2.
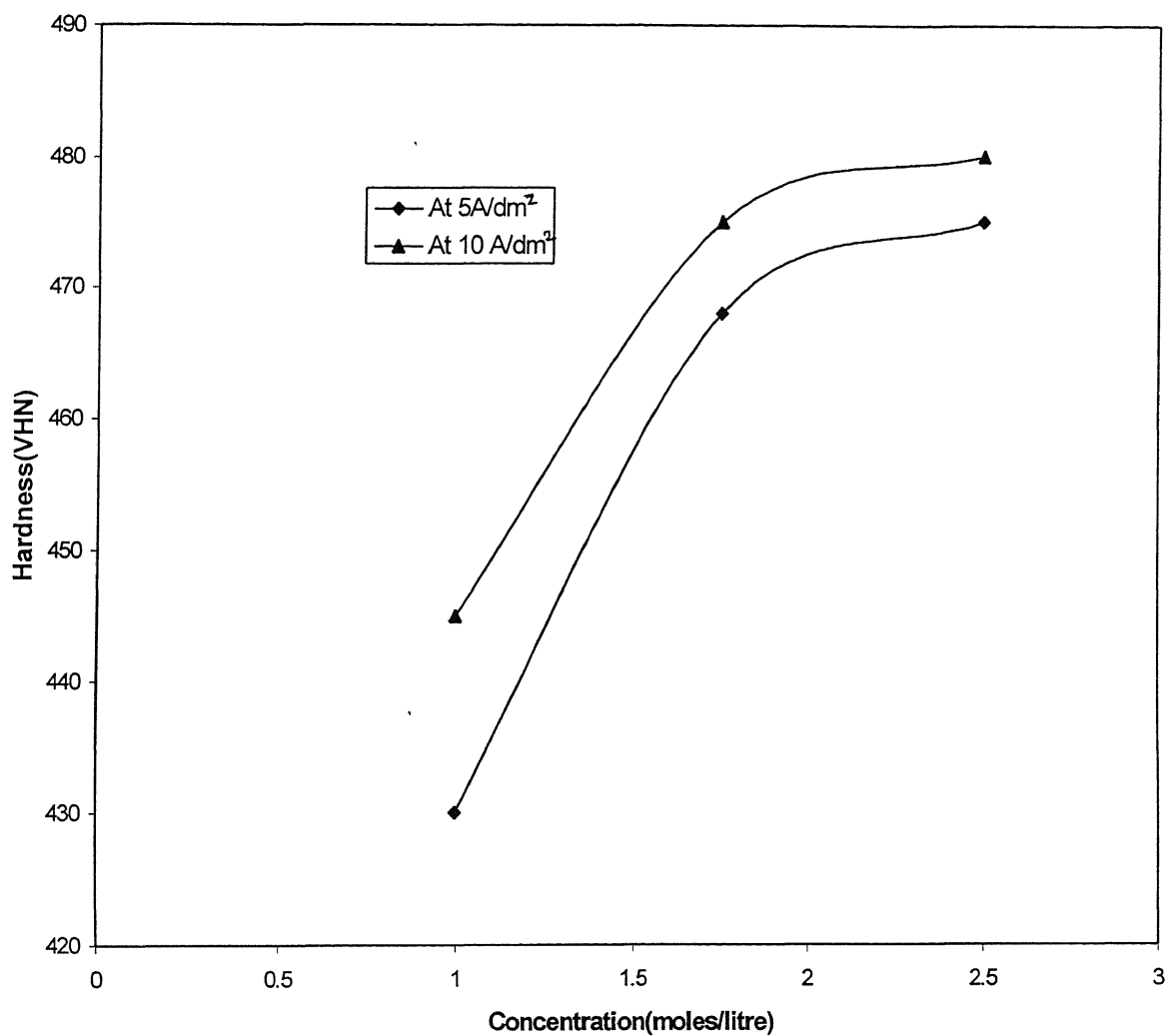
Figure 3.16 Variations in micro hardness values for different concentrations of malonic acid + oxalic acid(0.17 m/l) solution and current densities.

CHAPTER 4

CONCLUSIONS

1. These organic electrolyte mixtures result in the formation of uniform, integral colored films without any cracks on aluminum alloy of commercial purity.

2. Bath voltage required for anodizing in mixture of tartaric acid + oxalic acid bath, maleic acid + oxalic acid bath and malonic acid + oxalic acid bath is less as compared to tartaric acid bath, maleic acid bath and malonic acid bath.

3. Anodic oxide film with hardness values ranging from 375 to 475 VHN are formed at room temperature(30^0C) by utilizing these electrolytes.

4. The coating ratio was found to be higher for higher concentrations of base acid and also for higher current densities.

5. Anodizing carried under stirring conditions results in formation of oxide coating of greater thickness and higher hardness than anodizing carried under non stirring conditions for similar operating parameters.

6. Mixture of malonic acid and oxalic acid seems to be decisively more corrosive than other organic electrolyte mixture used.

7. Coating thickness was found to be greater with increase in current density.

Comparison between the values of coating thickness obtained by measurement (under microscope), by weighing and by Faraday's law in Malonic(1.0 mole/l) + Oxalic acid(0.17 mole/l) bath at 5 A/dm^2 current density:

S No.	Anodizing time (minutes)	Weight of oxide coating (grams)	Weight calculated by Faraday's law (grams)	Measured Thickness (microns)	Calculated Thickness (microns)	
					By weight of oxide film	By Faraday's law
1	30	0.0589	0.155	16	30.5	77.5
2	40	0.0792	0.2072	21	39.6	103.6
3	50	0.0959	0.259	27	47.05	129.5
4	60	0.1107	0.3108	35	55.35	155.4
5	70	0.1175	0.3626	43	60	180

By Faraday's law:

Weight of oxide coating = {(Mol. Wt. Of alumina × current(A) × time(Sec.))/ (96500×n)}

Where, n = 3. Current = 0.25 A at 5 A/dm^2 and 0.5 A at 10 A/dm^2 .

Area = 5 cm^2.

Thickness (t) = {(Weight of coating)/ (Area × Density of alumina)}

Where,
Density of alumina = 3.98.

Comparison between the values of coating thickness obtained by measurement (under microscope), by weighing and by Faraday's law in Malonic(1.0 mole/l) + Oxalic acid (0.17 mole/l) bath at 10 A/dm^2 current density:

S No.	Anodizing time (minutes)	Weight of oxide coating (grams)	Weight calculated by Faraday's law (grams)	Measured Thickness (microns)	Calculated Thickness (microns)	
					By weight of oxide film	By Faraday's law
1	10	0.0597	0.1036	14	30	51.8
2	20	0.0833	0.2072	21	41.65	103.6
3	30	0.1077	0.3108	32	53.85	155.4
4	40	0.1448	0.4145	43	72.4	207
5	50	0.1567	0.518	56	78.35	260
6	60	0.1946	0.621	70	97.3	310.5

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